# The Intrinsic Role of Membrane Morphology to Reduce Defectivity in Advanced Photochemicals

*Authors: T. Kohyama, Kozue Miura, Yasushi Ohyashiki, Aiwen Wu*

## ABSTRACT

Defect source reduction in leading-edge iArF resists is a critical requirement to improve device performance and overall yield in lithography manufacturing processes. It is believed that some polar polymers can aggregate and be responsible for single or multiple micro-bridge defects. Further investigation into the formation of these defects is needed. We have previously presented the effective removal of gel-like polymers using nylon media.[1] However, as the industry is moving to smaller feature sizes, there is a need to further improve the defect removal efficiency. In this paper, a filter, comprised of a novel membrane called Azora™ with unique morphology and high-flow performance, is introduced. This new filter shows better on-wafer and gel removal performance in an advanced ArF solution than conventional nylon. In addition, it shows improved stability during chemical storage, unlike traditional media such as nylon and UPE media. Results and possible retention mechanisms are discussed.

## INTRODUCTION

It becomes even more important as the feature size of semiconductor devices continues to decrease, attaining sub-10 nm scales. Moreover, EUV lithography, new planarization processes, and new resist chemistries introduce new challenges in defect control. Filtration technology is an intrinsic part of the semiconductor manufacturing process to reduce defectivity, yet there are only a few types of filtration media used in the industry. Presently, several parameters are known to effectively assess filtration performance, including flow rate, membrane surface property, membrane structure, and surface properties.

For instance, it is well-known that an adsorption type filter membrane such as nylon is effective at removing polar polymers. On the other hand, particulate contaminants are often removed via sieving retention like that of UPE membranes. The optimization and improvement of membrane surface properties can enhance filtration performance, however, filtration technology innovation is still needed to meet the most recent defect targets.

In this paper, we present a membrane, Azora, with a morphology that is distinctly different from the most commonly used membranes in semiconductor filtration. With its unique morphology, the high-flow Azora membrane shows an excellent performance in on-wafer evaluations and gel removal capabilities. In addition, bottled ArF material filtered with Azora membrane shows improved latent defects performance and particle size variability when compared to UPE and nylon membranes.

## EXPERIMENTAL

### Flow Rate Performance

Flow rate as a function of differential pressure was measured comparing Azora and a typical asymmetric UPE membrane (comparable in pore size) in water. Tests were performed using 70 mm diameter 10-inch cartridge filter devices.

### On-wafer Evaluation

ArF polymer solution was bottled after filtration with an Optimizer-D™ filter device. The filtered solution was later dispensed on wafers at one week, one month, and two months post-bottling intervals to measure coating defects and the associated time dependencies. For bridge-type pattern defects, the filtered solution was evaluated two weeks after bottling.

## Flow Rate Performance

Filter flow rate performance is one of the most important factors responsible for improved productivity at bulk chemical suppliers, with higher flow rates (and associated lower pressure drops) being more desirable for throughput. Our recent study revealed that a higher pressure drop has a negative impact on defect performance due to the fact that sufficiently high enough pressure makes gels deform and thereby allows them to be squeezed through the membrane even after once captured by the filter. Therefore, to address the design goals of higher flow and lower pressure drop, Azora was developed to reduce pressure drop as much as possible through an increase in porosity as well as a reduction in membrane thickness, both enabled by its novel morphology. From Figure 1, it is clear that a 10″ cartridge with the Azora membrane has a 75% higher flow rate when compared to an asymmetric UPE membrane of similar pore size.

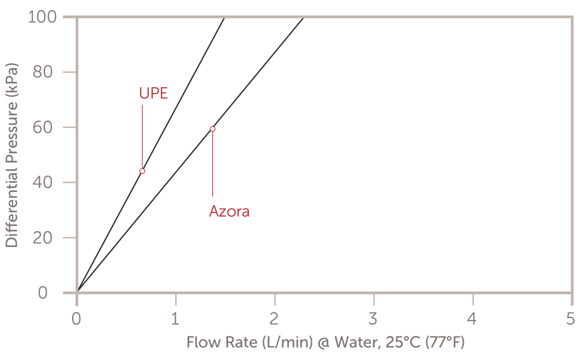


*Figure 1. Comparative flow rate performance.*

## On-wafer Evaluation

On-wafer evaluations are very useful to ultimately judge if filtration works to improve defectivity, as it is difficult to observe and confirm correlations between lab scale testing results and yield data at advanced nodes. In this study, metrology inspections for both post-coating and pattern defects were conducted.

The filter with Azora membrane produces different data on coating and pattern defects compared to those of UPE and nylon. The Azora filter had the fewest coating defect counts and least time-dependent variability compared to both nylon and UPE membrane filters that produced peak defect counts after one week of storage that somewhat decreased over time, but remained two orders of magnitude higher than that of Azora (Figure 2).

Interesting differences in time-dependent defect particle size were observed between the different types of filter membranes. Specifically, with UPE and nylon membranes, on-wafer latent defect counts from post-bottled solutions increased as a function of storage time, whereas defect particle count for solution filtered using Azora remained consistent, independent of post-bottling storage time. Similarly, for on-wafer microbridge defects, the same time-dependent defect size phenomena was confirmed for nylon but not observed for UPE (Figure 3). These observations introduce the possibility that the Azora membrane morphology may improve not only on-wafer defectivity, but also minimize the variability and latent defectivity of photoresist solutions post-bottling well beyond that of currently available asymmetric nylon and UPE membranes.

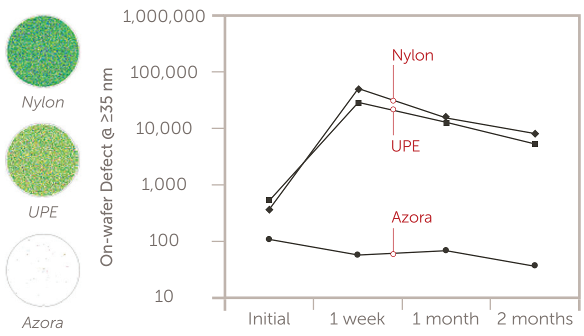


*Figure 2. Coating defects inspection.*

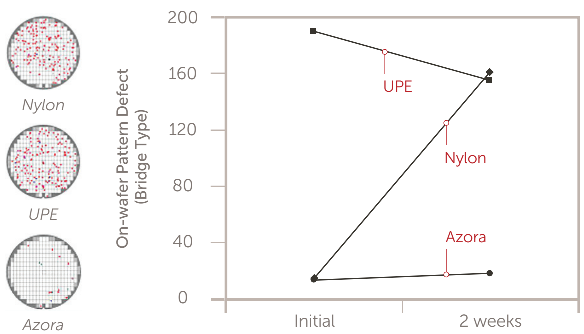


*Figure 3. Patterned defects inspection.*

## DISCUSSION

### Membrane Morphology

Membrane morphology is a key factor to determine filter performance, as it governs the manner in which particles/contaminants in a chemical will interact with the membrane. Figure 4 shows a schematic of three membrane architectures. The symmetric and asymmetric architectures are commonly encountered in both UPE and nylon membranes and both these architectures have some advantages/disadvantages. In recent times, as the filter pore sizes have become tighter, asymmetric membranes have become more common to compensate for the loss of flow which has resulted in the tightest layers becoming thinner. In contrast, the Azora membrane has a tortuous, complex structure which is very different from existing membranes. As shown in the results section, this unique morphology overcomes the flow loss issue at tighter pore sizes while being able to impart a new functionality to the membrane. Further investigation is required to understand the mechanism of reduction of latent defects/defects on wafer in ArF photoresist solutions – this will ultimately be useful in further optimization of the membrane.

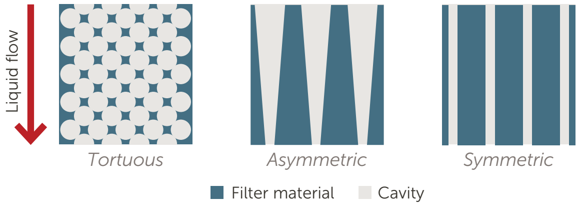


*Figure 4. Schematic of membrane architectures.*

### Current Hypothesis on Mechanism of Defect Reduction

Our current results suggest that the unique morphology of the high-flow Azora membrane helps in reduction of gel particles subsequently leading to reduction in both coating defects and microbridging defects. Though the exact mechanism needs further investigation, we hypothesize that when gel particles are in a continuously mixed bulk phase, such as in a solution at a bulk chemical manufacturer prior to filtration, there is negligible interaction (i.e., aggregation) between them, leading to relatively large interstitial spaces (Figure 5). This dispersion of gel particles creates a unique challenge for typical UPE and nylon membranes where there is possibly a limited interaction due to the symmetric/asymmetric morphology. Conversely, the tortuous path and the high flow of the Azora membrane increases the chance of interactions between (a) multiple gel particles in the microscopic porous spaces leading to aggregation and capture, and (b) the gel particles and membranes surface leading to their capture via Van der Waals forces. In our future experiments, we plan to further investigate this potential capture mechanism of gel particles allowing for novel filtration concepts and technology.

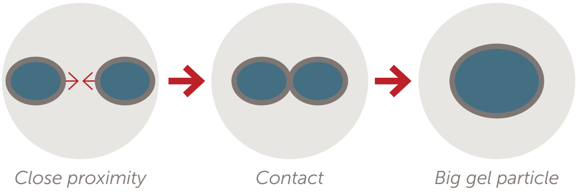


*Figure 5. Hypothesis regarding gel aggregation.*

## CONCLUSIONS

Current portfolio of filtration membranes including UPE and nylon have demonstrated satisfactory performance in reduction of gel particles from ArF polymer solutions. However, to successfully enable the high-volume manufacturing of semiconductor processes in the sub-10 nm nodes, we need a fundamental innovation in filter membrane technology to achieve the ever-reducing defect targets. In this study, a filter using the high-flow Azora membrane showed a unique functionality in reduction of gel particles in solution, attributed to its morphology, leading to on-wafer microbridge reduction and reduction in latent defects, especially in aged resist. The results provide a potentially multifaceted improvement to the bulk chemical manufacturers (from improved flow, improved chemical batch specifications, and increased shelf-life), as well as integrated device manufacturers (from reduced pressure drop and improved on-wafer performance).

## REFERENCES


1. Kohyama, T, *"The filter adsorption mechanism in photoresist materials"* Proc. SPIE 8325 (2012).



*This paper was originally presented at a 2018 SPIE Advanced Lithography poster session.*

## FOR MORE INFORMATION

Please call your Regional Customer Service Center today to learn what Entegris can do for you.
Visit entegris.com and select the Contact Us link to find the customer service center nearest you.

## TERMS AND CONDITIONS OF SALE

All purchases are subject to Entegris' Terms and Conditions of Sale. To view and print this information, visit entegris.com and select the Terms & Conditions link in the footer.

Entegris
PURE ADVANTAGE

Corporate Headquarters
129 Concord Road
Billerica, MA 01821
USA

Customer Service
Tel +1 952 556 4181
Fax +1 952 556 8022
Toll Free 800 394 4083